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<b>(54) Title:</b> HYDROGENATED NITRILE BUTADIENE RUBBER THERMOPLASTIC FLUOROPOLYMER BLEND  <b>(57) Abstract</b>  The present invention is related to a rubber compound comprising a mixture of from 40 to 99 % by weight of mixture of elastomer having a fully or unsaturated backbone; and from 1 to 60 % by weight based on said mixture of a thermoplastic fluoropolymer. The present invention is also directed to a rubber article as well as an impact modified plastic compound comprising the same mixture of elastomer and thermoplastic fluoropolymer.		

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HYDROGENATED NITRILE BUTADIENE RUBBER  
THERMOPLASTIC FLUOROPOLYMER BLEND

FIELD OF THE INVENTION

This invention deals with elastomeric materials comprised of a mixture of elastomers having a fully or unsaturated backbone and a fluoropolymer, the manufacture of such elastomeric materials, and their use for the manufacture of applications using such elastomeric materials.

BACKGROUND OF THE INVENTION

In the automobile industry, the octane rating of gasolines as well as optimizing the fuel efficiency is a major concern. As a result, the use of alcohols and aromatic hydrocarbons to increase the octane rating or fuel efficiency was utilized. An additional concern is the EPA's strict emission standards, which also must be followed.

It is known to use nitrile rubber for applications involving fuel, oil and heat resistance applications. It has been found that a straight hydrogenated acrylonitrilebutadiene (HNBR) polymer such as THERBAN (commercially available from Bayer AG) or ZETPOL (commercially available from Nippon Zeon Co.) and rubber copolymers using HNBR suffer from high volume change and high permeation when in contact with methanol containing fuels. In the designing of elastomeric parts for fuel contact, the volume change as well as the physical strength of the elastomer are measured whereby a sample specimen of an elastomeric part is fully immersed in oxygenated hydrocarbon fluid for certain timer periods and test temperatures appropriate to the finished part. Upon completion, test samples are removed from the fluid and retained strength and change in shape and volume are determined.

In light of EPA regulations, automakers measure the rate of permeation or loss of hydrocarbons and oxygenated hydrocarbons through all components in contact with fuel. Permeation is the rate of transmission

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of the hydrocarbon or oxygenated hydrocarbon through the cross-section of the part where the part is designed to contain the fluid.

In both cases, the desire is to maintain zero to low levels of permeation or hydrocarbon loss, low volume change and high part strength.

Various techniques for improving strength and hydrocarbon fluid resistance of compositions based on hydrogenated acrylonitrile butadiene and fluorinated polymers have been proposed.

Improving the resistance of THERBAN hydrogenated acrylonitrile butadiene is referenced in Buding, et al. (U.S. Patent No. 4,565,614) which shows resistance to hydrocarbon fuels when blending with vinylidene fluoride hexafluoropropylene tetrafluoroethylene terpolymers known in the industry as fluoroelastomers. These blends still suffer from high volume change when tested in oxygenated fuels such as 85% ASTM Fuel C/15% Methanol, as well as high permeation of the fuel through the HNBR/FKM blends. In addition, Buding, et al. requires a weight ratio of 70% FKM/30% HNBR to reduce volume change to 20% in ASTM Fuel C, which at the same time greatly reduces the tensile strength of the blend. Processing is an additional issue whereas the neat composition (polymer and curative only - no fillers, plasticizers, antidegradants or process aides) by Buding, et al. is rough and baggy on the mill, which makes the composition difficult to handle during manufacture.

New SAE J30 fuel hose standards have been adopted which call for a low permeation hose. The present invention provides a rubber compound, which may be used in fuel hoses to provide for a low permeation hose, which meets the new SAE standards. Additionally, the rubber compounds of the present invention may be used in applications having contact with fuel.

Surprisingly, the present invention greatly improves the resistance to Oxygenated Fuel as measured by volume change and permeation, as well as maintaining cured strength through all blend ratios. It enables mixtures with high HNBR content to be used. Processing is improved with

increased green strength allowing smoother extrudates and a reduction in part thickness for those skilled in the manufacture of hoses, as well as faster cycle time at a lower injection pressure for injection molded articles. Additionally, the milling characteristics of the invention described in the present invention provide excellent banding on the mill, no bagging, and smooth sheeting.

#### SUMMARY OF THE INVENTION

The present invention is related to a rubber compound comprising a mixture of from 40 to 99 % by weight of mixture of elastomer having a fully saturated or unsaturated backbone; and from 1 to 60% by weight based on said mixture of a thermoplastic fluoropolymer. The present invention can also be used in ratios typically used for plastic impact modification with such ratios comprising a mixture of from 1 to 40 by weight of elastomer having a fully saturated or unsaturated backbone and from 60 to 99% by weight based on said mixture of a fluoropolymer.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a graph of the tensile strength of a prior art mixture compared with the mixture of the present invention.

FIG. 2 shows a graph of the volume change of prior art mixture when compared with the mixture of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The task of the present invention is to manufacture a rubber compound which can be extruded or molded into an application which when used, is in direct contact with fuel, which may result in low permeation and low volume change.

Accordingly, in the rubber compound, a mixture of an elastomer having a fully saturated or unsaturated backbone with a mixture of a thermoplastic fluoropolymer is used.

The elastomer having a fully saturated backbone, i.e. elastomer wherein a continuous path can be traced from one end of the elastomer polymer to the other without going through a double bond, which can be

employed in the present invention are LEVAPREN® ethylene acetate copolymers and hydrogenated acrylonitrile butadiene commercially available from Bayer Corporation and Bayer AG as THERBAN and from Nippon Zeon Co. as ZETPOL), chlorosulfanated polyethylene, chlorinated polyethylene, alkylated chlorosulfonated polyethylene, and ethylene acrylic polymers (commercially available from DuPont and DuPont Dow), polyacrylate, epichlorohydrin and hydrogenated acrylonitrile butadiene (commercially available from Nippon Zeon). In a most preferred embodiment, fully saturated elastomers such as HNBR polymers are employed.

In the present invention, the elastomer may also have an unsaturated backbone. Such elastomers include acrylonitrile butadiene, chlorobutyl rubber, bromobutyl rubber, and polychloroprene. The elastomer is present in an amount from 40 to 99% by weight based on the mixture. In a preferred embodiment, the elastomer is present in an amount ranging from 50 to 75% by weight based on the mixture.

The viscosity of the hydrogenated acrylonitrile butadiene of the present invention ranges from 20 to 160 Mooney Units, preferably from 30 to 105, more preferably from 50 to 105 and most preferably, from 65 to 105 Mooney Units. The acrylonitrile content of the hydrogenated acrylonitrile butadiene of the present invention ranges from 15 to 50% and more preferably, from 38 to 50%. The residual double bond of the hydrogenated acrylonitrile butadiene of the present invention ranges from 0.1 to 50%, preferably from 0.1 to 25% when the viscosity ranges from 30 to 105 Mooney Units, more preferably from 0.1 to 18% when the viscosity ranges from 50 to 105 Mooney Units and most preferably from 0.1 to 10% when the viscosity ranges from 65 to 105 Mooney Units. For an acrylonitrile butadiene copolymer, the viscosity ranges from 25 to 105 Mooney Units and more preferably, from 70 to 105 Mooney Units.

The thermoplastic fluoropolymers, which can be employed in the present invention can be, for example: polytetrafluoroethylene, tetrafluoroethylene propylene copolymer, fluorinated ethylene propylene

copolymer, polytetrafluoroethylene perfluorovinylether copolymer, ethylene tetrafluoroethylene copolymer, polyvinylidene fluoride, polyvinylidene fluoride hexafluoropropene copolymer, polychlorotrifluoroethylene, ethylene chlorotrifluoroethylene copolymer, or polyvinylidene dichloride.

5 The molecular weights of such fluoropolymers range from 10,000 to 10,000,000, the fluorine content ranges from 20 to 72% by weight and the melting point ranges from 125 to 347°C. In a most preferred embodiment, polyvinylidene fluoride hexafluoropropene copolymer is used.

10 Conventional ingredients of a rubber mixture, which are known to one skilled in the art, can be used. These ingredients may include, for example, fillers, plasticizers, antidegradants, process aides, pigments, acid acceptors and vulcanization chemicals such as peroxides and coagents, or sulfur, sulfur donors, vulcanization accelerators, and vulcanization  
15 retarders. The weight percent of each rubber ingredient can change to accommodate various article requirements. The present invention can use any combination of the above-ingredients, or simply the polymer mixture and vulcanization chemicals such as peroxides and accelerated sulfur and sulfur donor systems.

20 The rubber compound of the present invention may be employed in applications in which high resistance to a range of hydrocarbon and oxygenated fuels are required. Such applications may be used in such industries such as petroleum exploration, extraction and refining, petroleum distribution as well as automotive and aerospace. In particular,  
25 such applications are fuel hoses, fuel tubing, fuel bladders, diaphragms, seals, gaskets, timing belts and O-Rings.

Additionally, an impact modified plastic compound comprising the above-mentioned elastomer and mixture of a thermoplastic fluoropolymer is also the subject of the present invention. Such plastic compounds may  
30 be used in film, solid pipe, lined pipe, lined vessels, pumps, molded parts, fabrics, and tubing. The elastomer is present in an amount ranging from 0.5 to 40% by weight based on the mixture. In a preferred embodiment,

the elastomer is present in an amount ranging from 2 to 25% by weight based on the mixture. The fluoropolymer is present in a range from 60 to 99.5% by weight based on the mixture, preferably from 75 to 98% by weight.

- 5           For impact modification, fluoroplastics can be polymerized with propylene, hexafluoropropane and other monomers. Using THERBAN HNBR, the comonomer can be replaced to effectively yield increased impact resistance. These impact-modified fluoroplastics can be used neat, or compounded with fillers, plasticizers, antidegradants, process aides and  
10       pigments.

The following examples serve to clarify the invention.

#### EXAMPLES

In the examples, which follow, the following materials were used:

- A)   Thermoplastic Fluoropolymer: a copolymer of vinylidene fluoride  
15   and hexafluoropropane with a glass transition of -38 C and flex modulus between 620 to 1240 MPa.
- B)   THERBAN HNBR: Hydrogenated Acrylonitrile Butadiene copolymer having an acrylonitrile content of 43% by weight, a degree of hydrogenation of 99%, and a Mooney Viscosity ML @ 100 C (1+4 min) of  
20   72 commercially available from Bayer AG.
- C)   Fluoroelastomer: Fluorine rubber having a fluorine content of 70% by weight, a specific gravity of 1.91, and a Mooney Viscosity ML @ 121°C (1+4) of 55 to 70.
- D)   Polymeric Adipate: ester-based plasticizing oil.
- 25   E)   Carbon Black N990.
- F)   Acid Acceptor: Magnesium Oxide.
- G)   Vulcanization agent 1: 2,5 dimethyl-2,5-bis(t-butyl peroxy) hexane 40% active.
- H)   Vulcanization agent 2: Triallylisocyanurate.
- 30   I)   Vulcanization agent 3: Dicumyl peroxide 40%.



Example 1

904 grams of hydrogenated acrylonitrile butadiene, 271 grams of carbon black N990, and 27.1 grams of magnesium oxide are introduced into a 1.5 liter mixer fitted with dual rotors and temperature control for the body and rotors. The ingredients are mixed at 77 RPM until the temperature of the mixture reaches 160°C with discharge onto a mill at 30°C where 27.1 grams of triallyl isocyanurate and 90.4 grams of 2,5 dimethyl-2,5-bis (t-butyl peroxy)hexane (40% active) are added with the final mixture homogenized and sheeted.

Example 2

780 grams of hydrogenated acrylonitrile butadiene, 260 grams of FKM fluorinated terpolymer, 312 grams of carbon black N990, and 31.2 grams of magnesium oxide are introduced into a 1.5 liter mixer fitted with dual rotors and temperature control for the body and rotors. The ingredients are mixed at 77 RPM until the temperature of the mixture reaches 160°C with discharge onto a mill at 30°C where 31.2 grams of triallyl isocyanurate and 31.2 grams of 2,5 dimethyl-2,5-bis (t-butyl peroxy)hexane (40% active) are added with the final mixture homogenized and sheeted.

Example 3

577 grams of hydrogenated acrylonitrile butadiene, 192 grams of polyvinylidene fluoride copolymer, 577 grams of carbon black N990, 77 grams of magnesium oxide, 77 grams of polyester adipate, 7.7 grams of stearic acid, 3.1 grams of zinc salt of methyl mercaptobenzimidazole, and 38.5 grams of zinc oxide are introduced into a 1.5 liter mixer fitted with dual rotors and temperature control for the body and rotors. The ingredients are mixed at 77 RPM until the temperature of the mixture reaches 160°C with discharge onto a mill at 30°C where 11.5 grams of triallyl isocyanurate and 57.7 grams of dicumyl peroxide (40% active) are added with the final mixture homogenized and sheeted.

Example 4

454 grams of hydrogenated acrylonitrile butadiene, 195 grams of polyvinylidene fluoride copolymer, 713 grams of carbon black N990, 65 grams of magnesium oxide, 130 grams of polyester adipate, 6.5 grams of stearic acid, 2.6 grams of zinc salt of methyl mercaptobenzimidazole, and 32.5 grams of zinc oxide are introduced into a 1.5 liter mixer fitted with dual rotors and temperature control for the body and rotors. The ingredients are mixed at 77 RPM until the temperature of the mixture reaches 160°C with discharge onto a mill at 30°C where 9.7 grams of triallyl isocyanurate and 48.7 grams of dicumyl peroxide (40% active) are added with the final mixture homogenized and sheeted.

Example 5

410 grams of hydrogenated acrylonitrile butadiene, 273 grams of polyvinylidene fluoride copolymer, 751 grams of carbon black N990, 68 grams of magnesium oxide, 102 grams of polyester adipate, 6.8 grams of stearic acid, 2.7 grams of zinc salt of methyl mercaptobenzimidazole, and 34 grams of zinc oxide are introduced into a 1.5 liter mixer fitted with dual rotors and temperature control for the body and rotors. The ingredients are mixed at 77 RPM until the temperature of the mixture reaches 160°C with discharge onto a mill at 30°C where 10.3 grams of triallyl isocyanurate and 51.2 grams of dicumyl peroxide (40% active) are added with the final mixture homogenized and sheeted.

Example 6

337 grams of hydrogenated acrylonitrile butadiene, 337 grams of polyvinylidene fluoride copolymer, 742 grams of carbon black N990, 67 grams of magnesium oxide, 168 grams of polyester adipate, 6.8 grams of stearic acid, 2.7 grams of zinc salt of methyl mercaptobenzimidazole, and 34 grams of zinc oxide are introduced into a 1.5 liter mixer fitted with dual rotors and temperature control for the body and rotors. The ingredients are

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mixed at 77 RPM until the temperature of the mixture reaches 160°C with discharge onto a mill at 30°C where 10 grams of triallyl isocyanurate and 51 grams of dicumyl peroxide (40% active) are added with the final mixture homogenized and sheeted.

Table 1

Example	1	2	3	4	5	6
Terban HNBR	100	75	75	70	60	50
Thermoplastic Fluoropolymer	0	0	25	30	40	50
FKM	0	25				
N990	30	30	75	110	110	110
Acid Acceptor	3	3	10	10	10	10
Polymeric Adipate			10	20	15	25
Zinc Oxide			5	5	5	5
Stearic Acid			1	1	1	1
Zinc Salt of methyl mercaptobenzimidazole			0.4	0.4	0.4	0.4
2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane 40% active	10	3				
Dicumyl peroxide 40% active			7.5	7.5	7.5	7.5
Triallylisocyanurate	3	3	1.5	1.5	1.5	1.5
Properties						
Hard Shore A2 Inst. (pts)	62	63	78	84	88	91
Tensile Strength, Mpa	13.3	15.8	14.8	11.6	13	9.4
Elongation @ break, %	195	215	340	270	140	175
25% modulus, MPa			2.2	3.5	5.4	6.2
100% modulus, Mpa	7.2	8.7	3.5	8.8	12.4	10
Green strength, Mpa			5.6	4.7	5.3	3
Swelling in 85% fuel C/15% MeOH 3 days @ RT (% by volume)	80.8	69.8	47.4	45	40	25
Permeation in same fuel, g/m <sup>2</sup> /d			224	302	220	175
TR 10 (temperature retraction, C)	-16	-15	-13	-19	-17	-17

Surprisingly, the addition of vinylidene fluoride fluoroplastic dramatically increased green strength of hydrogenated acrylonitrile without reducing green elongation at break. In comparison with the mixture disclosed in Buding, et al., there is no requirement of preblending with other  
5 rubber compounding ingredients. This remarkable compatibility allows the use of the mixture in a "neat" composition whereas the mixture and vulcanization ingredients are combined and cured. The manufacture of parts is simplified since no carbon black is required. Hoses can be extruded without a mandrel in the green or uncured state thereby eliminating two (2)  
10 steps from the from the manufacturing process (manufacture of the mandrel, and subsequent removal of the mandrel from the vulcanized hose). The mixture in Buding, et al. would still require the use of a mandrel for hose manufacture.

Even more surprising are the present mixture's low temperature  
15 properties. Plastic materials usually impart high stiffness at low temperature. Therefore, part manufacturers select elastomers to maintain flexibility. The THERBAN/fluoroplastic mixture departs from normal rubber and plastic mixtures and shows similar low temperature properties as compared to an all elastomer mixture. In comparison to the mixture of Buding, et al. (Example 2  
20 in Table 1), the low temperature properties of the THERBAN/fluoropolymer mixtures are equal or better based on ASTM Temperature Retraction tests (TR 10).

Figure 1 illustrates the strength of the cured mixtures of the present invention at various ranges of percent THERBAN in the mixture when  
25 compared with a mixture using FKM (Buding, et al.) In all THERBAN weight percentages, the strength is equal or superior to the mixture disclosed in Buding, et al. The advantage in strength is apparent when the fuel resistance is compared in Figure 2.

Figure 2 illustrates the benefits of the mixture of the present invention  
30 when compared with the mixture of Buding, et al. From the figure, as the weight % of THERBAN in either FKM or PVDF increases, the volume change of the mixture increases. Using PVDF, the volume change

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increases at a much slower rate allowing increased weight percent of THERBAN depending on the application requirements. Compounders use the increased weight percent of THERBAN to lower the finished part cost: the higher the THERBAN content, the lower the material cost. Additionally, 5 whereas the compositions based on 25 wt% THERBAN with FKM have lower strength, the compositions based on PVDF have higher strength. change, whereas only 25% by weight of THERBAN can be used in Buding, et al. This results in tensile strength of 20 MPa for the described mixture versus 14 MPa for Buding, et al., which is greater than a 40% 10 improvement in strength.

The described mixture of the present invention exhibits many other comparable rubber properties required for elastomer part manufacture. Therefore, such mixtures are suitable for the production of hoses, seals, and other articles. In particular, they are suitable when exacting requirements 15 are imposed in regard to green and cured strength, and oxygenated fuel resistance, for example, fuel hose, fuel seals, and gaskets and other elastomeric parts exposed to direct fuel contact.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely 20 for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

WHAT IS CLAIMED IS:

1. A rubber compound comprising a mixture of:
  - (a) from 40 to 99% by weight based on said mixture of an elastomer having a fully saturated or unsaturated backbone; and
  - 5 (b) from 1 to 60% by weight based on said mixture of a thermoplastic fluoropolymer.
2. A rubber compound according to Claim 1 wherein said elastomer has a fully saturated backbone.
3. A rubber compound according to Claim 2, wherein said  
10 elastomer is selected from the group consisting of ethylene acetate copolymer, chlorosulfanated polyethylene, chlorinated polyethylene, alkylated chlorosulfonated polyethylene, ethylene acrylic polymers, polyacrylate, epichlorohydrin and hydrogenated acrylonitrile butadiene (HNBR).
- 15 4. A rubber compound according to Claim 3, wherein said elastomer is hydrogenated acrylonitrile butadiene.
5. A rubber compound according to Claim 1, wherein said elastomer has a viscosity ranging from 20 to 160 Mooney Units; an acrylonitrile content ranging from 15 to 50% and a residual double bond  
20 ranging from 0.1 to 50%.
6. A rubber compound according to Claim 5, wherein said elastomer has a viscosity ranging from 30 to 105 Mooney Units; an acrylonitrile content ranging from 15 to 50% and a residual double bond ranging from 0.1 to 20%.
- 25 7. A rubber compound according to Claim 6, wherein said elastomer has a viscosity ranging from 50 to 105 Mooney Units; an acrylonitrile content ranging from 15 to 50% and a residual double bond ranging from 0.1 to 18%.
8. A rubber compound according to Claim 7, wherein said  
30 elastomer has a viscosity ranging from 65 to 105 Mooney Units; an acrylonitrile content ranging from 15 to 50% and a residual double bond ranging from 0.1 to 10%.

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9. A rubber compound according to Claim 1, wherein said elastomer contains an unsaturated backbone.

10. A rubber compound according to Claim 9 wherein said elastomer is selected from a group consisting of bromobutyl, chlorobutyl,  
5 polychloroprene, or acrylonitrile butadiene rubber.

11. A rubber compound according to Claim 1, wherein said thermoplastic fluoropolymer is a copolymer of vinylidene fluoride and hexafluoropropene.

12. A rubber compound according to Claim 1, wherein said  
10 thermoplastic fluoropolymer is a homopolymer of difluoroethene.

13. A rubber compound according to Claim 1, wherein said rubber compound also comprises additives such as: fillers, plasticizers, antidegradants, process aides, pigments, acid acceptors, and vulcanization chemicals.

14. A rubber article comprising a rubber compound comprising a  
15 mixture of:

(a) from 40 to 99% by weight based on said mixture of an elastomer having a fully saturated or unsaturated backbone; and

(b) from 1 to 60% by weight based on said mixture of a  
20 thermoplastic fluoropolymer.

15. A rubber article according to Claim 14, wherein said elastomer is hydrogenated acrylonitrile butadiene (HNBR).

16. A rubber article according to Claim 14, wherein said elastomer has a viscosity ranging from 20 to 160 Mooney Units; an  
25 acrylonitrile content ranging from 15 to 50% and a residual double bond ranging from 0.1 to 50%.

17. A rubber article according to Claim 14, wherein said thermoplastic fluoropolymer is a copolymer of vinylidene fluoride and hexafluoropropene.

18. A rubber article according to Claim 14, wherein said rubber  
30 article is a hose.



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19. A rubber article according to Claim 14, wherein said rubber article is a seal.

20. A rubber article according to Claim 14, wherein said rubber article is a gasket.

5 21. A rubber article according to Claim 14, wherein said rubber article is a molded part.

22. An impact modified plastic compound comprising a mixture of:

10 (a) from 0.5 to 40% by weight based on said mixture of an elastomer having a fully saturated or unsaturated backbone; and

(b) from 60 to 99.5% by weight based on said mixture of a thermoplastic fluoropolymer.

23. An impact modified plastic compound according to Claim 22, wherein said elastomer is hydrogenated acrylonitrile butadiene (HNBR).

15 24. An impact modified plastic compound according to Claim 23, wherein said elastomer has a viscosity ranging from 20 to 160 Mooney Units; an acrylonitrile content ranging from 15 to 50% and a residual double bond ranging from 0.1 to 50%.

20 25. An Impact modified plastic compound according to Claim 22, wherein said thermoplastic fluoropolymer is a copolymer of vinylidene fluoride and hexafluoropropene.

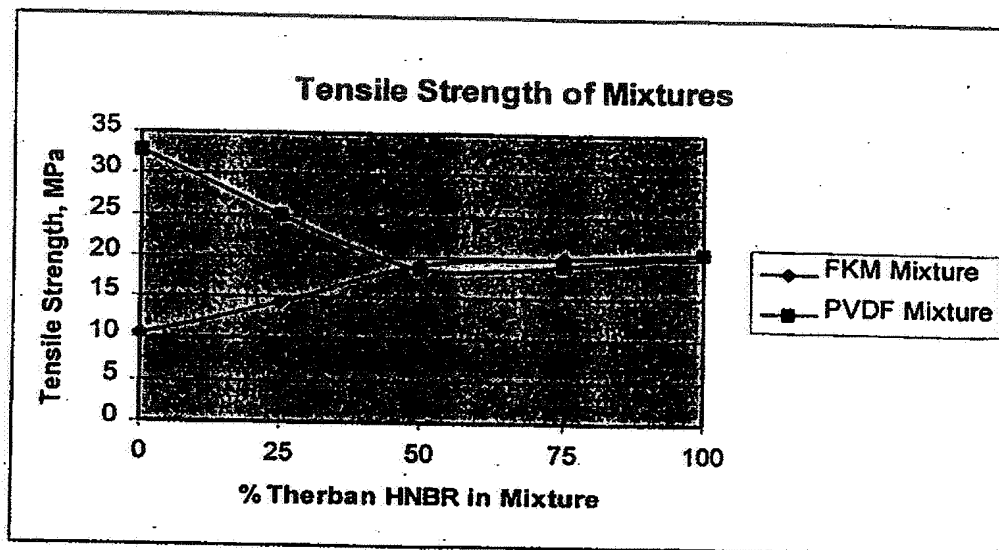


FIGURE 1

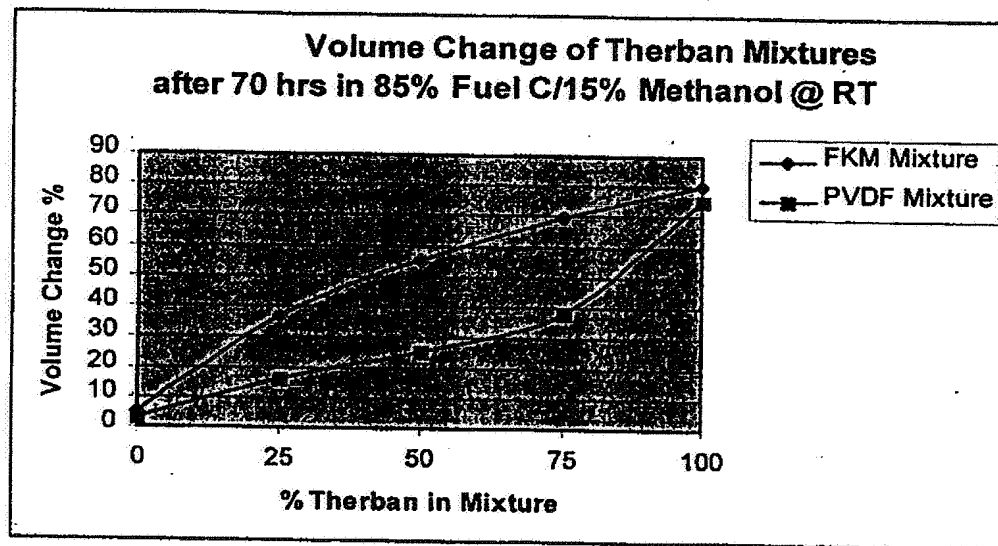


FIGURE 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/08107

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L21/00 C08L27/12 C08L15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 194 030 A (JAPAN SYNTHETIC RUBBER CO LTD) 10 September 1986 (1986-09-10) page 4, line 27 - page 5, line 17; claims 1,14 page 14, line 12 - line 25 page 21, line 2 - line 15 ---	1-21
X	EP 0 428 158 A (DAIKIN IND LTD) 22 May 1991 (1991-05-22) page 3, line 5 - line 6; claims ---	1-17, 21-25
X	EP 0 854 173 A (ATOCHEM ELF SA) 22 July 1998 (1998-07-22) page 2, line 25 - line 32; claims 1,5,10 page 3, line 51 - line 52 ---	1-25
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

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